Bulk and surface electronic structure of lanthanide metals

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Abstract

Recent systematic work on the electronic structure of lanthanide metals in the bulk and at the surface by high-resolution photoemission (PE) using synchrotron radiation and by inverse photoemission (IPE) with tunable photon energy is reviewed. In this way both the occupied and the unoccupied electronic states can be studied. The observed phenomena include the occurrence of d-like surface states on close-packed surfaces of the lanthanide metals, the variation of surface core-level shifts of $4f^{n-1}$ PE (electron-removal) and $4f^{n+1}$ IPE (electron-addition) states, a separation of surface core-level shifts into initial-state and final-state contributions, as well temperature-dependent exchange splitting of unoccupied d-band states and the d-like surface state in ferromagnetic Gd metal.

Keywords: Electronic structure; Lanthanide metals; Gadolinium

1. Introduction

The electronic structure of lanthanide metals both in the bulk and at the surface is relatively unexplored from the experimental point of view, partly owing to the earlier difficulties in preparing atomically clean and well ordered surfaces of these materials in monocrystalline form. This is also the reason why much of the earlier surface work on lanthanide metals suffered seriously from surface contamination problems [1]. Since it became clear that lanthanide metals can be grown epitaxially on W(110) [2], the situation has substantially changed with the possibility of preparing monocrystalline films in situ in a straightforward way. On the theoretical side, there has been early work on the band structure of lanthanide metals [3,4], and more recently also on surface states [5], surface core-level shifts [6,7], and the magnetism of Gd metal [8]. Owing to the scarcity of reliable experimental results, however, the theoretical development has also been quite slow.

In this contribution, we report on some of the recent experimental progress in the study of the electronic structure of lanthanide metals using high-resolution photoemission (PE) and inverse photoemission (IPE) with variable photon energy. In particular we describe a systematic study of surface states on the close-packed (0001) surfaces of the heavy lanthanide metals as well as surface core-level shifts for the same surfaces and for Eu(110). With IPE, the surface states can be studied additionally in the unoccupied region above the Fermi level, and surface core-level shifts can be measured for the electron-addition ($4f^{n+1}$) states. A comparison of these latter shifts with the related surface core-level shifts of electron-removal ($4f^{n-1}$) states studied by PE allowed for the first time a separation of these shifts into initial-state and final-state contributions. Finally, we discuss briefly the temperature-dependent electronic structure of Gd(0001) in the bulk and at the surface, in particular the temperature-dependent magnetic exchange splitting of the unoccupied d-band and the temperature-induced changes in the position and the population of the d-like surface state of Gd.

2. Experimental procedures

The PE experiments were performed with a high-resolution spectrometer, based on a Leybold-Heraeus EA11 hemispherical electron-energy analyzer, employing either He-II radiation from a resonance lamp or synchrotron radiation from various beamlines at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY), in particular the high-performance SX700/II monochromator operated by the Freie Universität Berlin [9]. The total-system resolution varied between 25 and 150 meV (FWHM). The IPE measurements were carried out with an IPE spectrometer equipped with a toroidal-grating monochromator, a position-sensitive detector, and a Pierce-type electron gun [10]. The angle-resolved IPE spectra were recorded in the constant-initial-state mode with constant kinetic

energy of incoming electrons; the total-system resolution was about 250 meV (FWHM) for the IPE measurements.

The lanthanide metals were prepared in the form of monocrystalline thin films (approximately 100 Å thick) grown epitaxially on W(110) substrates, which had been cleaned before by the standard procedure. Various substrate temperatures during deposition and subsequent annealing were chosen depending on the specific lanthanide metal. The film thickness was monitored by a quartz microbalance, and the temperature of the sample was measured by an AlCr/NiCr thermocouple in contact with the W(110) crystal. In most cases, rather diffuse low energy electron diffraction (LEED) patterns were observed after deposition, which sharpened considerably on annealing of the films at elevated temperatures. Many of the spectra reported were taken with the samples cooled to temperatures as low as 20 K using either a closed-cycle He refrigerator or a liquid-He-cooled cold finger. To this end, a special sample holder had to be constructed that allowed the W(110) single crystal to be heated up to about 2000 K for cleaning and to be cooled down to about 20 K for the PE or IPE measurements. The base pressure in the various experimental chambers used was always in the 5×10^{-11} mbar range; these good ultrahigh vacuum conditions were found to be essential for maintaining clean surfaces during the measurements.

3. Surface states on close-packed surfaces

An occupied surface state on a lanthanide material was first observed by PE for the close-packed surface of Gd(0001) [11] and soon after modeled theoretically as a non-bonding state with δ_{z^2} character [5,12]. It was suggested that its occupancy might be connected with the magnetism of Gd metal, with a bulk Curie temperature of 292 K. Subsequently, an analogous d-like occupied surface state was reported for Tb(0001) in angle-resolved [13] as well as in high-resolution angle-integrated PE work [14]. We therefore explored the existence of an analogous surface state on the close-packed (0001) surface of a monocrystalline film (approximately 70 Å thick) of La metal grown epitaxially on W(110) [15]. The questions addressed were whether such surface states exist also for the light lanthanide metals as well as in the unoccupied region above the Fermi level E_F.

Fig. 1 displays PE spectra (left) and IPE spectra (right) of La(0001), recorded at normal emission of photoelectrons and normal incidence of primary electrons respectively. The PE and IPE spectra each show two prominent spectral features, labeled A and B for PE and A' and C for IPE. While peaks B and C at energies of about 1.5 eV below and above E_F respectively can be readily assigned to bulk features, peaks A and
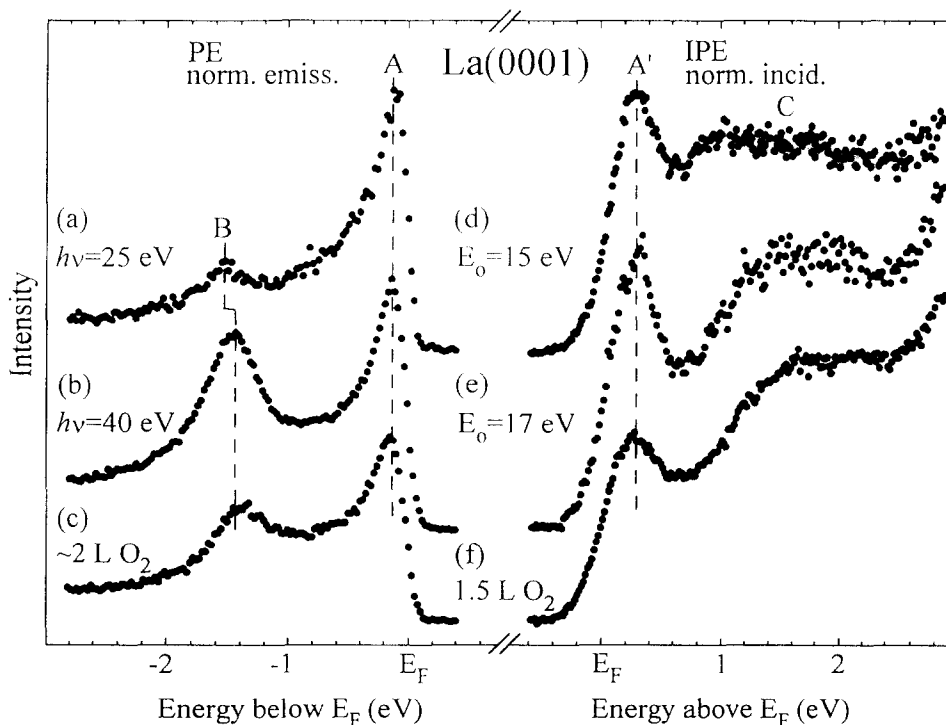

Fig. 1. Photoemission spectra (left) of La(0001) taken at (a) $h\nu = 25$ eV and (b) $h\nu = 40$ eV for a clean and well ordered surface; (c) after adsorption of approximately 2 Langmuir (1 L = 10^{-6} Torr × sec) O_2 taken at $h\nu = 40$ eV. The spectra are normalized to the same incident photon flux. Inverse photoemission spectra (right) taken at a primary-electron energy of (d) $E_0 = 15$ eV and (e) $E_0 = 17$ eV of a clean and well ordered La(0001) film; (f) IPE spectrum taken at $E_0 = 17$ eV after adsorption of 1.5 L O_2 (from Ref. [15]).
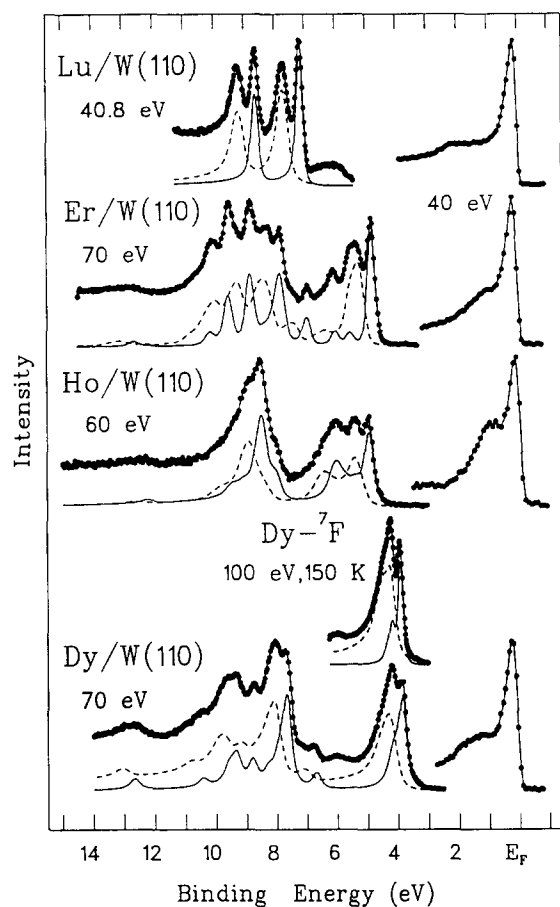
Fig. 2. Photoemission spectra taken from the (0001) faces of mono-crystalline films of Dy, Ho, Er, and Lu metal grown epitaxially on W(110). The spectra were taken at the given photon energies, with the samples at room temperature; for Dy metal, the shallowest 4f-multiplet component was also measured with the sample cooled to 150 K. Note the intense PE peaks from surface states very close to the Fermi level observed in all cases. The results of least-squares fit analyses are given by the solid lines through the data points as well as by the solid and dashed subspectra respectively, representing the 4f-multiplet spectra from the bulk and from the topmost surface layer (from Ref. [19]).

A' lie directly at E_F in the region of a wide gap in the bulk-band structure along the ΓA direction [16]. As was shown in Ref. [15] (see also spectra (a)/(b) and (d)/(e), respectively, in Fig. 1), the two peaks A and A' do not disperse with the crystal momentum perpendicular to the surface $k_\perp$, and in particular peak A' can be quenched by O_2 adsorption; it is not clear at present why peak A seems to quench less well (see Fig. 1). These observations identify peaks A and A' as spectral signatures of the occupied and empty part, respectively, of a surface state located directly at E_F. In addition, the photon-energy dependence of the PE cross-section of feature A, measured for photon energies up to 100 eV, rules out a 4f-related character of this state and favors a 5d origin [15].

Occupied surface states on close-packed surfaces of lanthanide metals were also observed by PE for Tm

and Yb metals [17,18], as well as for Dy, Ho, Er, and Lu metals [19]. Spectral signatures of these surface states are clearly seen in the normal-emission PE spectra taken with 40 eV photons, which are displayed in the right part of Fig. 2. In all cases, very narrow and occupied surface states were observed at E_F; the measured photon-energy dependences of the PE-cross sections support again a 5d-like character in all cases [19], in agreement with the theoretical prediction for Gd(0001). In addition to La(0001), the unoccupied parts of the surface states have also been investigated for Gd(0001) [20] (see below) and Tb(0001) [21]. It is now clear that such a d-like surface state exists directly at the Fermi level on the close-packed surfaces of all heavy lanthanide metals as well as on La(0001) and Nd(0001) [22]; it thus has to be considered to be a common property of close-packed surfaces of lanthanide metals.

4. Surface core-level shifts

Next, we discuss the subject of surface core-level shifts of the $4f^{n-1}$ electron-removal states reached by PE for the close-packed surfaces of the heavy lanthanide metals as well as Eu(110). Surface shifts of core-level PE lines were first observed more than a decade ago for Au metal [23]. They are due to the reduced coordination of surface atoms and can be related to the difference in cohesive energies of the initial and final states [24]. In the case of lanthanide materials, particularly well resolved surface shifts are observed for the 4f PE lines due to relatively narrow intrinsic line-widths [25]. The subject was considered to be fairly closed, when a few years ago a self-consistent-field linear-muffin-tin orbitals calculation with the atomic-spheres approximation claimed very good agreement between theory and experiment [26]; this calculation considered only initial-state contributions to the surface core-level shifts. However, a recent high-resolution PE study of a well ordered (0001) surface of a mono-crystalline film of Tb metal produced a surface core-level shift δ_s that was more than a factor of 2 smaller than the previously reported experimental and theoretical values [14]; this renewed the interest in surface core-level shifts for lanthanide metals.

Fig. 3 displays high-resolution normal-emission PE spectra of Tb(0001) in the binding-energy (BE) region from E_F to the leading $^8S_{7/2}$ component of the $4f^7$ final-state PE multiplet, recorded with 48 eV photons and the metal film at $T = 150$ K [14]. Spectrum (a) was taken from the film grown at a substrate temperature of 150 K, while spectrum (b) was recorded after the film had been annealed for 2 min at $T = 900$ K. The doublet at a binding energy (BE) of about 2.5 eV originates from emission to the $4f^7$-$^8S_{7/2}$ final state; it is split into a bulk component at a BE of about 2.3
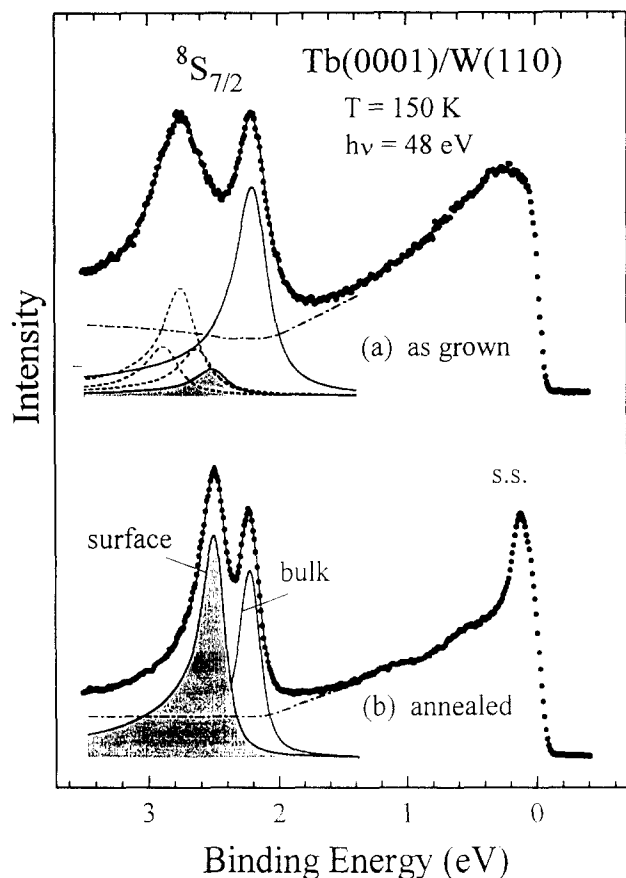
Fig. 3. PE spectra in the region of the leading $^8S_{7/2}$–4f^7 multiplet component of a 130 Å thick Tb(0001) film grown epitaxially on W(110): (a) as grown at $T = 150$ K; (b) after annealing for 2 min at $T = 900$ K. The solid lines through the data points represent the results of a least-squares fit analysis. While spectrum (b) is well described by a doublet of Doniach–Sunjic lines from the bulk (solid) and the surface (shaded), spectrum (a) is decomposed into four components from surface atoms with coordination 9 (shaded), as well as 8, 7, and 6 (short-dashed) (from Ref. [14]).

eV and a surface component shifted by the surface core-level shift to higher BE. It is striking that the surface core-level shift changes by more than a factor of 2 on annealing of the Tb(0001) film, and the surface component narrows down to almost the width of the bulk component. Similarly interesting is the change in the conduction-band emission just below E_F. On annealing of the Tb(0001) film, a narrow peak appears just below E_F, which is assigned to the above-discussed δ_{z^2}-like surface state; without annealing, the as-grown film shows just a triangular-shaped conduction-band emission characteristic of polycrystalline surfaces of lanthanide metals [25]. These observations, as well as the sharp LEED pattern observed for the annealed Tb(0001) film, can be taken as strong evidence for an atomically smooth, well ordered Tb(0001) surface. The small surface core-level shift observed for the well annealed surface was thus assigned to atoms at surface sites with coordination 9, while the larger shift observed

for the as-grown film was explained by a substantial fraction of low-coordinated surfaces sites at steps and corners [14].

The spectra in Fig. 3 were least-squares fitted by a superposition of Doniach–Sunjic-shaped lines [27], for PE from the bulk (coordination number $Z = 12$) and from surface atoms with various coordination numbers from 9 to 6, superimposed on an integral background from inelastic electron scattering and the triangular-shaped emission from the conduction band (dash-dotted line). Within the framework of a simple tight-binding model, the following relation between the surface energy shift for coordination N and the shift for coordination Z was assumed to hold [28]:

$$\delta_Z/(1 - \sqrt{Z/12}) = \delta_N/(1 - \sqrt{N/12}) \tag{1}$$

The model spectra were finally convoluted by a Gaussian to simulate finite experimental resolution. The results of this analysis for the leading $^8S_{7/2}$ PE component are shown in Fig. 3 by the solid curve through the data points; the subspectra, corresponding to contributions from the differently coordinated sites, are also given. While the as-grown film contains surface sites with coordinations 9 (shaded), as well as 8, 7, and 6 (short-dashed), the spectrum of the well annealed Tb(0001) film can be described by only a single surface component in addition to the bulk component. This leads to a surface core-level shift of $\delta_s = -(0.26 \pm 0.03)$ eV for a smooth close-packed Tb(0001) surface. It is striking that the magnitude of this δ_s value is smaller by more than a factor of 2 than those of previously published experimental [25] and theoretical values [26]. The negative sign for δ_s means that the surface component is shifted to lower energy with respect to the bulk component, i.e. to higher binding energy; the chosen sign convention is in agreement with that of Ref. [29].

The findings for Tb(0001) prompted a renewed systematic study of surface core-level shifts for smooth surfaces of monocrystalline lanthanide metals. Fig. 4 displays the high-resolution PE spectrum taken from the (110) surface of a 100 Å thick monocrystalline film of Eu(110) grown on W(110); the formation of the (110) face was confirmed by LEED [19]. Note the individual ^7F_J multiplet components in the bulk spectrum of the 4f^6 final state, which could be resolved for the first time. The spectrum from the topmost surface layer (dashed subspectrum) is less well resolved and is again shifted to higher binding energies by the surface core-level shift; by least-squares fit, a surface core-level shift of $\delta_s = -(0.48 \pm 0.03$ eV) was derived [19].

Similar measurements were performed on well ordered monocrystalline films of Yb(111) and Tm(0001) [18] as well as on the (0001) surfaces of Dy, Ho, Er, and Lu metal (see Fig. 2, spectra on the left side) [19]. The 4f^{n-1} final-state PE multiplet spectra in Fig. 2 were analyzed on the basis of a superposition of a bulk
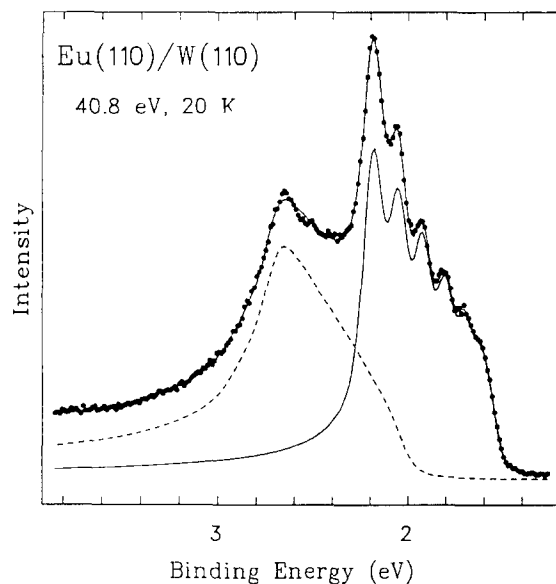
Fig. 4. High-resolution PE spectrum of the (110) surface of a monocrystalline film of b.c.c. Eu metal at 20 K taken with He-II radiation. The film was grown on W(110). Note that the individual components of the bulk subspectrum are resolved (from Ref. [19]).

Fig. 5. Gd-4f MCD-PE spectrum of a remanently magnetized 110 Å thick Gd(0001) film on W(110) at $T = 25$ K taken with approximately 45% circularly polarized 47 eV photons. Photon spin and sample magnetization formed an angle of 18°; the experimental geometry is given in the inset. For the analysis, the (0001) surface layer (shaded) was assumed to be ferromagnetically aligned to the bulk of Gd (solid curve). The dash-dotted curve represents the integral background (from Ref. [29]).

spectrum (solid subspectrum) and a shifted surface spectrum (dashed subspectrum) in each case. The simplest 4f multiplet is observed for Lu(0001), with a $4f^{14}$ configuration in the initial state and one 4f hole in the PE final state. It consists of two spin-orbit doublets, one from the bulk and one from the topmost surface layer, which are separated by $\delta_s = -(0.53 \pm 0.02)$ eV.

An accurate value for δ_s of Gd(0001) could only be obtained owing to lack of resolution, by making use of the recently discovered magnetic circular dichroism (MCD) in 4f PE from ferromagnetic lanthanide materials [30,31]. Fig. 5 shows the MCD-PE spectrum of a remanently magnetized approximately 110 Å thick Gd(0001) metal film on W(110) at 25 K recorded with about 45% circularly polarized 47 eV photons from the U2-SGM beamline at BESSY. Photon spin and sample magnetization formed an angle of 18°. This orientation causes a more pointed shape of the unresolved $4f^6$ final-state PE multiplet [30], which in turn leads to a well resolved peak in the leading edge in the case of high spectrometer resolution [29]. The fit results in a rather accurate value for $\delta_s = -(0.29 \pm 0.03)$ eV [29].

Fig. 6 gives a graphical representation of the surface core-level shifts of $4f^{n-1}$ electron-removal states of the heavy lanthanide metals from Eu to Lu [19]. In addition to the described recent experimental results for well ordered surfaces of monocrystalline films (filled circles), previous experimental values measured for polycrystalline films (open circles, Ref. [25]) are also plotted. The open rhombs represent the results of an ab initio calculation for the (0001) faces of the lanthanide metals [26]; the open square represents the more recent the-
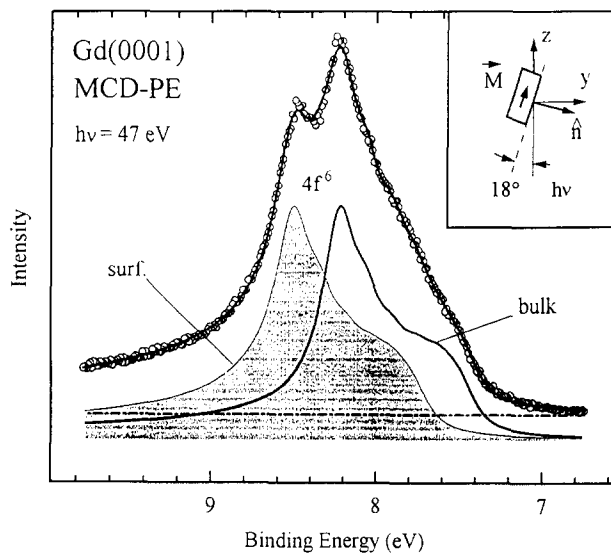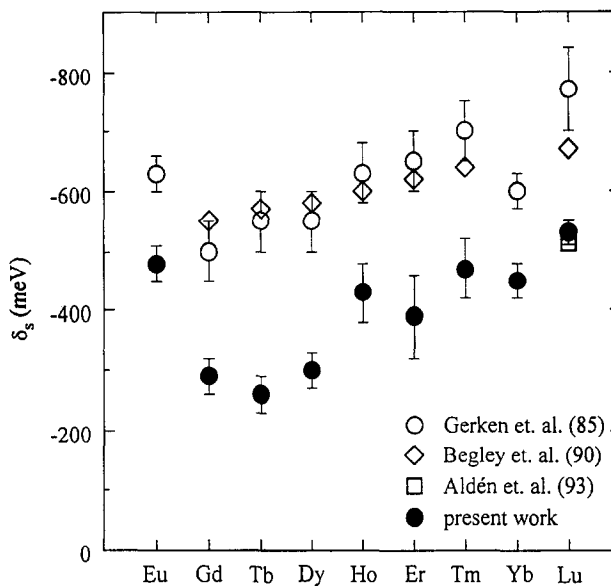

Fig. 6. Surface core-level shifts of $4f^{n-1}$ electron-removal states for the heavy lanthanide metals. In addition to the new results for monocrystalline films (filled circles), previous experimental values obtained on polycrystalline films by Gerken et al. (open circles, Ref. [25]) are included. The open rhombs represent the results of an ab-initio calculation for the (0001) faces of the lanthanide metals (Ref. [26]). The open square gives the theoretical value for Lu(0001) of a more recent calculation by Aldén et al. [7] (from Ref. [19]).

oretical value for Lu(0001) by Aldén et al. [7] which is in good agreement with the experimental result. Note that the δ_s values for the smooth (0001) faces of the lanthanide metals exhibit an overall increase in mag-

nitude from Gd to Lu; they are however, strikingly smaller than the previously published experimental results for polycrystalline metal films as well as the theoretical values of Begley et al. [26]. The δ_s value for the Eu(110) surface deviates from the systematics for the close-packed surfaces. This is in agreement with theoretical prediction [32] and experimental observations for other materials [33], which show that the δ_s values are usually smaller in magnitude for close-packed surfaces than for more open surfaces.

5. Initial and final-state contributions to surface core-level shifts

The striking discrepancy between the results of Begley et al. [26] and the experimental values for close-packed surfaces (see Fig. 6) suggests final-state contributions to δ_s, since only initial-state contributions had been considered in the calculations of Ref. [26]. In this respect, we briefly discuss a very recent study of surface shifts of $4f^{n+1}$ electron-addition states δ_s^{ea} (populated by IPE) and $4f^{n-1}$ electron-removal states δ_s^{er} (reached by PE) in Gd(0001) [29], where a separation of the observed δ_s values into initial-state and final-state contributions was achieved.

The feasibility of measuring surface core-level shifts of electron-addition states by IPE was first demonstrated for the case of La metal [34]. A typical IPE spectrum of the clean surface of a polycrystalline sample of La metal is shown in Fig. 7(a); for comparison, a Bremsstrahlung isochromat spectroscopy (BIS) spectrum, taken from Ref. [35], is also shown in (b). The IPE spectrum reveals, in addition to a step-like shape at E_F and a relatively structureless spectral shape due to transitions into unoccupied valence-band states, a relatively sharp and intense $4f^1$ signal at about 5 eV above E_F. This is split into two components, B from bulk La atoms and S from surface atoms. Comparison with the bulk-sensitive BIS spectrum shows that component B coincides in energy with the bulk La $4f^1$ IPE peak at 5.2 eV above E_F, while peak S is shifted by about -0.6 eV, i.e. toward E_F. The validity of this interpretation has been checked by quenching of the surface feature S through exposure to O_2 and to approximately 1 monolayer (ML) of Yb [34].

La has essentially no localized 4f electrons in the ground state, with the consequence that δ_s^{er} cannot be measured for the 4f shell. Therefore, the authors of Ref. [29] selected Gd(0001) for an accurate comparison of δ_s^{ea} and δ_s^{er} in order to investigate a possible contribution from final-state effects to δ_s. Fig. 8 displays IPE spectra of (a) a clean Gd(0001) film and (b) Gd(0001) covered by approximately 1.5 ML of Yb metal. The spectrum of clean Gd(0001) contains four spectral peaks denoted by A, B, C, and D. On Yb deposition,
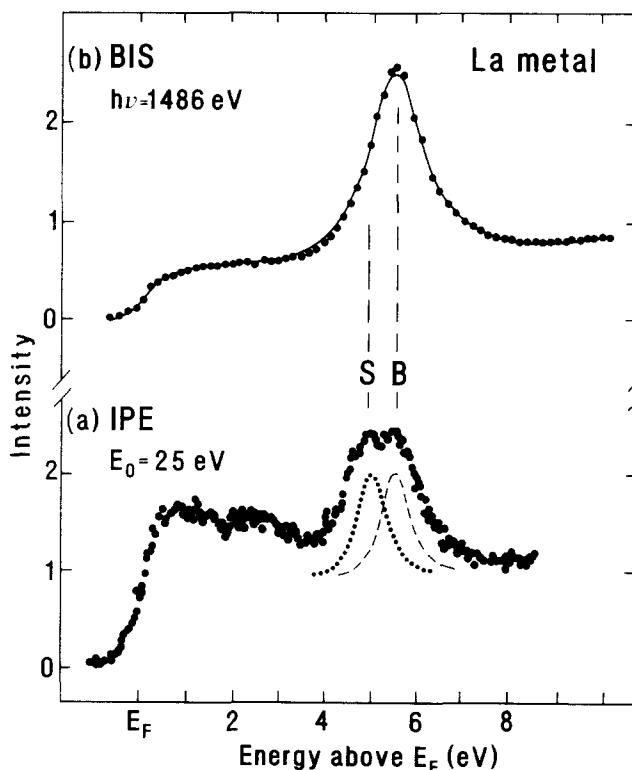

Fig. 7. (a) Inverse photoemission spectrum of La metal taken at a primary-electron energy of $E_0 = 25$ eV. (b) The corresponding BIS spectrum, taken at $h\nu = 1486$ eV (from Ref. [35]) is shown for comparison (from Ref. [34]).

structure B is completely quenched, and structure C is considerably weakened; in addition, peak A is shifted to a lower energy. This means that coverage of the surface by Yb metal selectively quenches the surface-related 4f signal (shaded subspectrum). Feature A has been assigned to an image-potential surface state [29]. A quantitative analysis by least-squares fit, taking the $4f^8-^7F_J$ multiplet (vertical-bar diagram in Fig. 8) into account, resulted in a surface shift of $\delta_s^{ea} = -(0.48 \pm 0.04)$ eV, where the negative sign denotes a shift toward E_F, i.e. to lower energies. In Ref. [29] the surface core-level shift for the electron-addition state of Gd(0001) δ_s^{ea} was compared with the analogous surface shift of the electron-removal state, $\delta_s^{er} = -(0.29 \pm 0.03)$ eV. First, the different magnitudes of δ_s^{er} and δ_s^{ea} show clearly that final-state effects exist, since the initial-state contributions $\delta_s(i)$ have to be identical in the two cases; note that PE and IPE start from the same initial state. If final-state effects are identified with the screening of the oppositely charged final states (core hole in PE, extra electron in IPE), the final-state contributions, $\delta_s^{er}(f)$ and $\delta_s^{ea}(f)$, can be assumed to be identical in magnitude, but opposite in sign in the two cases [29]. This leads to the two equations:

$$\delta_s^{er} = \delta_s(i) + \delta_s^{er}(f) = -0.29 \text{ eV} \tag{2}$$

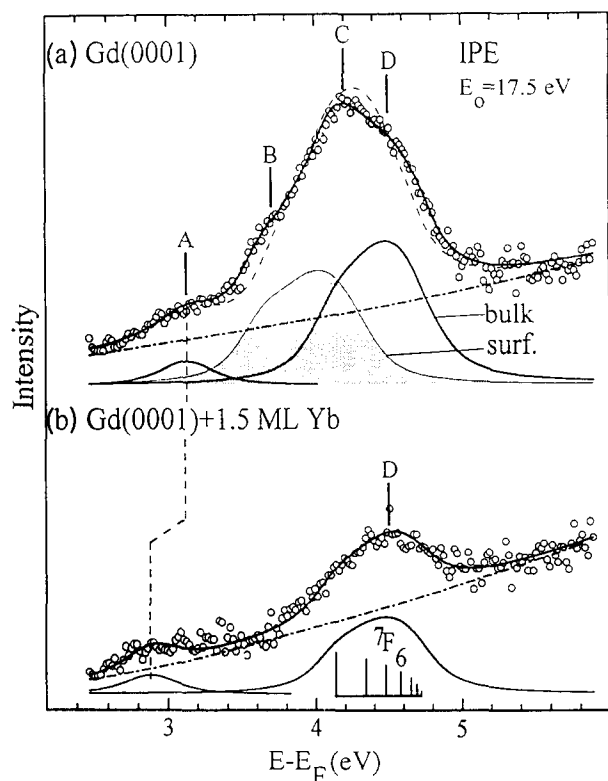$$\delta_s^{ea} = \delta_s(i) - \delta_s^{er}(f) = -0.48 \text{ eV} \tag{3}$$

Fig. 8. IPE spectra of Gd(0001) in the region of the $4f^8$ electron-addition state, taken at a primary-electron energy of $E_0=17.5$ eV: (a) clean Gd(0001) surface; (b) after exposure to 1.5 ML of Yb metal. Spectral features B, C, and D of clean Gd(0001) originate from $4f^8$ electron-addition states in the topmost surface layer (shaded) and in the bulk (solid curve); the vertical-bar diagram in (b) gives the energies and relative intensities of the individual ^7F_J bulk multiplet components. The solid curves through the data points in (a) and (b) represent the results of the best least-squares fits. The dashed curve in (a) was obtained in a fit where $\delta_s^{ea} = \delta_s^{er}$ was assumed; for details see text (from Ref. [29]).

which result in $\delta_s(i) = -0.38$ eV, $\delta_s^{er}(f) = +0.10$ eV, and $\delta_s^{ea}(f) = -0.10$ eV. This result clearly shows that, even though the dominant contribution to δ_s stems from the initial-state effect, final-state screening contributions cannot be neglected in a correct description of surface core-level shifts even for metal surfaces. The obtained signs for $\delta_s^{er}(f)$ and $\delta_s^{ea}(f)$ show that the PE and IPE final states are more effectively screened in the topmost Gd(0001) surface layer than in the bulk. This can be considered to be a consequence of the highly localized d-like surface states, since localized electrons are expected to screen more effectively than itinerant electrons. Even though not measured, similar surface effects can be expected for the close-packed surfaces of most of the lanthanide metals, where d-like surface states are abundant, as we have seen. It should be noted that recent improved calculations of surface core-level shifts for lanthanide metals also take final-state contributions into account [7,36].

6. Exchange splitting of bulk and surface states in Gd(0001)

There is presently considerable interest in the electronic and magnetic surface properties of ferromagnetic lanthanide metals owing to their prospectively unique yet widely unexplored magnetic properties. It was recently reported that Gd(0001) exhibits an enhancement of the surface ordering temperature by about 60 K as well as a slightly canted out-of-plane surface magnetization [37,38]. The conduction bands play an essential role for the exchange coupling between the localized 4f electrons, and they are spin-polarized, with an exchange splitting of approximately 0.6 eV [39]. A temperature-dependent exchange splitting of the bulk occupied 5d-band states has been found recently by PE [40]. It can be expected therefore that the unoccupied states of Gd(0001), both in the bulk and at the surface, also exhibit a temperature-dependent exchange splitting.

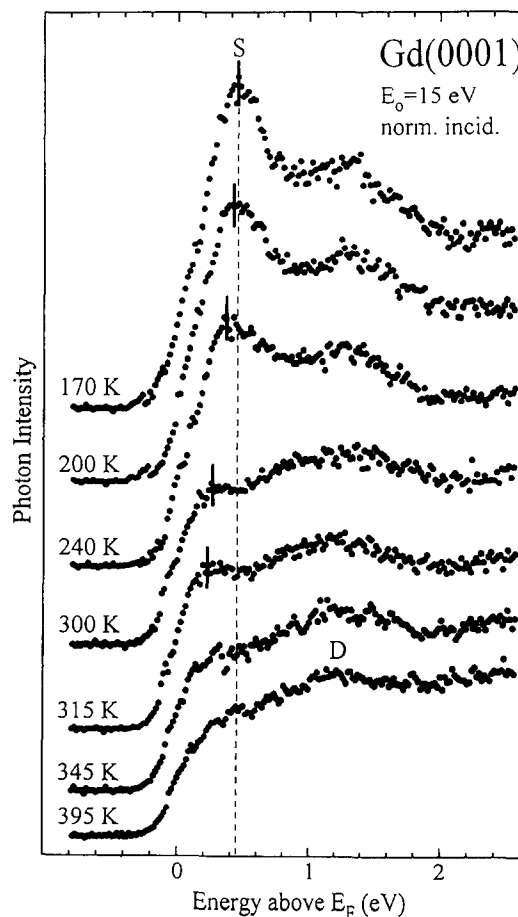Fig. 9 displays normal-incidence angle-resolved IPE spectra of Gd(0001) recorded with a primary-electron

Fig. 9. Normal-incidence inverse photoemission spectra of Gd(0001) recorded for temperatures between 170 K and 395 K. The position of the surface-state peak at 170 K is given by the dashed vertical line; it changes with temperature as indicated by the vertical bars (from Ref. [20]).

energy of $E_0 = 15$ eV for the given substrate temperatures [20]. The bottom spectrum, recorded at 395 K well above the highest recorded surface Curie temperature [37], can be considered as representative of paramagnetic Gd(0001). It reveals step-like behavior at E_F and a spectral feature D at about 1.2 eV above E_F, corresponding to the empty 4d-derived band.

Lowering of the sample temperature leads to two major changes in the IPE spectra of Fig. 9. (i) A peak S appears close to E_F, which is assigned to an empty band-derived surface state. This peak starts to be clearly discernible at 315 K. With further lowering of the temperature, it shifts to higher energies and gains spectral weight until it finally turns into a prominent peak for temperatures below 240 K. (ii) Feature D experiences a considerable broadening until, below 240 K, it begins to overlap with peak S. In analogy with the observations in Ref. [40] with respect to the occupied 5d-band, the observed broadening of the unoccupied 5d-band was attributed in Ref. [20] to exchange splitting into a majority-spin subband shifted towards E_F and a minority-spin subband shifted to higher energies.

For a quantitative analysis, the IPE spectra of Fig. 9 were least-squares fitted using a common parameter set for all spectra of the temperature series. The results of this analysis, described in more detail in Ref. [20], are shown for four representative spectra in Fig. 10 in form of solid curves through the data points plus solid and dotted subspectra that represent the empty 5d-band and the unoccupied surface state respectively. The inset in Fig. 10 displays the exchange splitting of the unoccupied 5d-band Δ_{ex} which decreases monotonically from $\Delta_{ex} = 0.78 \pm 0.15$ eV at 170 K to $\Delta_{ex} = 0.32 \pm 0.1$ eV at 345 K. Note that Δ_{ex} does not seem to vanish at the bulk Curie temperature of Gd, but rather about 55 K above. In addition, the spin-minority surface state S was found to move, with increasing temperature, monotonically to lower energies towards E_F; while it is mainly unoccupied at 300 K, it becomes half-filled only well above T_c^b.

These observations may well carry a clue to an improved understanding of the enhanced surface magnetism of Gd(0001), as was pointed out in Ref. [20]. Since it is known that the coupling of the local 4f moments in bulk Gd is strongly influenced by d electrons at E_F [41], the increasing occupancy of the d-like surface state in the temperature range above the bulk Curie temperature may well be responsible for the enhanced surface Curie temperature of Gd(0001).

7. Summary and conclusions

We have described recent progress in the experimental study of bulk and surface electronic properties of lanthanide metals, mainly on the basis of studies of well ordered monocrystalline metal films grown epitaxially on W(110) substrates. The systematics of surface core-level shifts of electron-removal states measured by PE for close-packed surfaces is in agreement with recent calculations taking initial and final-state contributions to surface energy shifts into account. We also described recent IPE work on surface shifts of electron-addition states and showed that these shifts, in combination with PE results for surface shifts of electron-removal states, allow an experimental separation of surface core-level shifts into initial-state and final-state contributions. The systematic occurrence of δ_{z^2}-like localized surface states close to the $\bar{\Gamma}$-point of the surface Brillouin zone of close-packed surfaces of lanthanide metals was discussed as well as the temperature-dependent exchange splitting of d-band states and the d-like surface state in the case of ferromagnetic Gd metal. It was argued that the occupancy of this surface state could well play an essential role in the enhanced surface magnetism of Gd(0001).
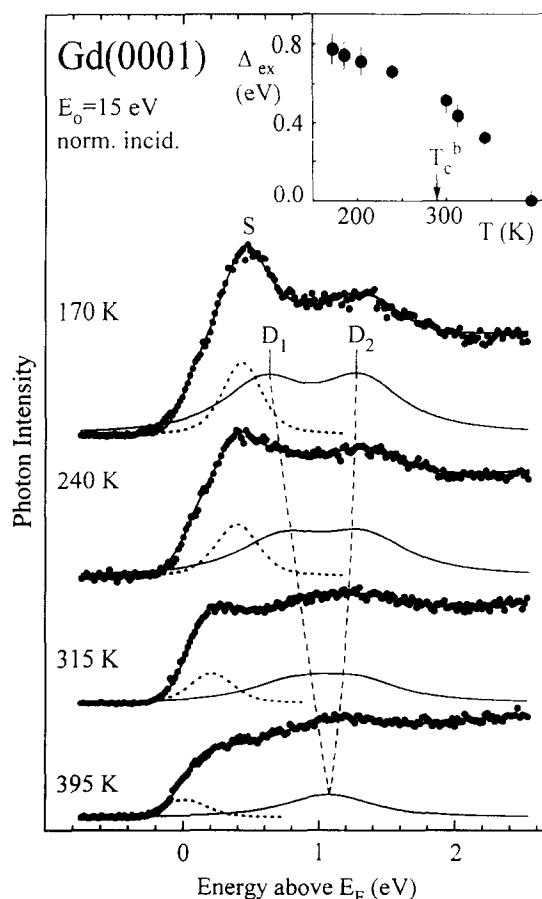

Fig. 10. Least-squares fit analysis of selected inverse photoemission spectra of Gd(0001) from Fig. 9 (for details, see text). The inset gives the exchange splitting Δ_{ex} as a function of temperature (from Ref. [20]).

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